Chapter 2

Review of Literature

2.1 GROUNDWATER

Water is perhaps the most precious asset on earth. People in several parts of the world are faced with the challenge to protect water and environment. Groundwater is one of the most important natural resources and accounts for more than 90 percent of water supply resources in many developing countries. It provides drinking water to communities, supports industry, agriculture, sustains streams and wetlands. About half the population in the world relies on groundwater as a source of drinking water. Rapid growth of urban areas has affected the groundwater quality due to over exploitation of resources and improper waste disposal. Indiscriminate discharge of domestic sewage, industrial waste, storm runoff and solid waste not only pollutes natural resources but also disturbs the subsurface flow of water and the harmonious relationship between the biotic and abiotic components of the ecosystem. Due to its mobility and ability to transport, transform and absorb pollutants ground water is becoming one of the most potentially dangerous contaminating media.

The natural quality of groundwater depends upon the physical environment, the origin and movement of water. Groundwater quality is mainly controlled by the type of human influence, the geochemical, the physical and the biological processes occurring in the ground and the existing hydrogeological conditions. Table 2.1 shows the processes that occur in ground water. Although the natural processes (listed in Table 2.1) may reduce groundwater contamination, many contaminants remain essentially unchanged after entering the groundwater body. Thus, detrimental effects at a location may persist for years, decades or centuries. Longer periods are often required for contaminants to be removed from aquifers (Zaprorozec, 1981; Carter et al. 1987).
Table 2.1. Natural processes controlling human influence on groundwater quality (Vrba and Zaporozec 1994)

<table>
<thead>
<tr>
<th>Geochemical processes</th>
<th>Physical processes</th>
<th>Biochemical processes</th>
<th>Biophysical processes</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acid-base reactions</td>
<td>Advection/convection</td>
<td>Cell synthesis</td>
<td>Filtration of pathogens</td>
</tr>
<tr>
<td>Adsorption-desorption</td>
<td>Dispersion</td>
<td>Organic decomposition</td>
<td>Transport of pathogens</td>
</tr>
<tr>
<td>Complexation</td>
<td>Evaporation</td>
<td>Transpiration</td>
<td>----</td>
</tr>
<tr>
<td>Oxidation-reduction</td>
<td>Filtration</td>
<td>----</td>
<td>-----</td>
</tr>
<tr>
<td>Solution-precipitation</td>
<td>Gas transport</td>
<td>----</td>
<td>----</td>
</tr>
<tr>
<td>---</td>
<td>Radioactive decay</td>
<td>----</td>
<td>----</td>
</tr>
</tbody>
</table>

2.2 SOURCES OF GROUND WATER CONTAMINATION

Ground water contamination occurs in three ways

a) Originating on the ground surface

b) Above the water table

c) Below the water table

2.2.1 GROUNDWATER CONTAMINATION THAT ORIGINATES ON THE GROUND SURFACE

i) Infiltration of contaminated surface water: Contamination originates from the disposal of municipal or industrial waste which directly enters into streams which are induced into adjacent aquifers causing pollution in ground water.

ii) Land disposal of solid and liquid waste material: Disposal of waste materials directly on to the land surface. Various examples are manures, sludge, garbage and industrial waste leading to pollutant infiltration.

iii) Impact of agriculture in groundwater
a) Organic fertilizers: Fertilizers (manure or slurry) may become a source of non-point groundwater pollution. Uncontrolled spillages of liquid waste for manure stock piles into groundwater produce point pollution. The extensive use of fertilizers is considered to be a main non-point source of nitrate that leaches to groundwater (Postma et al. 1991; Baker, 1992; Hubbard and Sheridan, 1994; Chowdary et al. 2005).

b) Pesticides: These include herbicides, fungicides and insecticides. These applications can act as sources of contamination to groundwater supplies serving large populations.

iv) Stock piles, tailing and spoils: Unprotected storage of de-icing salt (sodium and calcium) commonly mixed with sand causes these salts to slowly trickle down and pollute the groundwater. Also dumping of mining waste for cleaning and ore concentration usually generates acid water after rain and contaminates the groundwater.

v) Disposal of sewage and waste treatment plant and sludge: Sludge is the residue of chemical, biological and physical treatment of municipal and industrial wastes. It occurs also from contamination resulting from infiltration of partly treated waste water that has not undergone sufficient alteration.

vi) Animal feed lots: Feed lots for cattle, hogs, sheep and poultry provide huge value of waste. These wastes seep into the ground and contaminate the groundwater with large concentrations of nitrates, phosphates, bacteria etc.

2.2.2 GROUNDWATER CONTAMINATION ORIGINATING ABOVE THE WATER TABLE:

i) Septic tanks: In areas where the density of septic tanks is unusually high and the soils are permeable, this form of waste disposal causes ground water contamination. Septic tank systems contribute nitrate pollution of groundwater (MacQuarrie et al. 2001).

ii) Waste disposal excavation: Traditionally unattended excavations are often used as unregulated dumps which become sources for the infiltration of contaminants.

iii) Artificial recharge: Water used for artificial recharge consisting of storm runoff, excess irrigation water, stream flow, cooling water and treated sewage effluent.
iv) Landfills: Municipal and industrial wastes were disposed off in unlined open dumps. Leachates generated from waste decomposition and infiltration of precipitation and surface runoff spread into the subsurface causing contamination.

v) Leakage from underground storage tanks: Underground storage tanks are used for storing billions of gallons of liquids for municipal, industrial and agricultural purposes. Leakage due to corrosion of tanks causes contamination. Gasoline leakage is a wide-spread problem.

vi) Leakage from underground pipelines: Thousands of miles of buried pipelines exist to transport liquids. Leakage of these lines generally difficult to detect, cause extensive contamination.

vii) Surface impoundments: Surface impoundments including ponds and lagoons consist of shallow excavations and are used to dispose of agricultural, municipal and industrial wastes. Many of these impoundments have been located in permeable soils causing extensive infiltration of soluble waste constituents into the subsurface.

2.2.3 GROUNDWATER QUALITY PROBLEMS THAT ORIGINATE BELOW THE WATER TABLE

i) Agricultural drainage wells and canals: Drainage wells are vertical cased holes in the ground. They allow water to drain into more permeable materials. This drainage water usually contains agricultural chemicals and bacteria polluting the groundwater.

ii) Mines: Pumping of mine water to the surface by leaching the spoiled material etc will leads to infiltration of contaminated water to the deepest level.

U.S. Congress Office of Technology Assessment (1984) has compiled sources of groundwater contamination which is shown in Table 2.2. The man-made sources in Table 2.2 are according to the activity for which they were originally designed.
<table>
<thead>
<tr>
<th>Category I - Sources designed to discharge substances</th>
<th>Category IV - Sources discharging substances as consequence of other planned activities</th>
</tr>
</thead>
<tbody>
<tr>
<td>Subsurface percolation (e.g., septic tanks and cesspools)</td>
<td>Irrigation practices (e.g., return flow)</td>
</tr>
<tr>
<td>Injection wells</td>
<td>Pesticide applications</td>
</tr>
<tr>
<td>Hazardous waste</td>
<td>Fertilizer applications</td>
</tr>
<tr>
<td>Non-hazardous waste (e.g., brine disposal and drainage)</td>
<td>Surface mine-related</td>
</tr>
<tr>
<td><strong>Category II - Sources designed to store, treat, and/or dispose of substances; discharge through unplanned release</strong></td>
<td><strong>Category V - Sources providing conduit or inducing discharge through altered flow patterns</strong></td>
</tr>
<tr>
<td>Landfills</td>
<td>Production wells</td>
</tr>
<tr>
<td>Industrial hazardous waste</td>
<td>Oil (and gas) wells</td>
</tr>
<tr>
<td>Industrial non-hazardous waste</td>
<td>Geothermal and heat recovery wells</td>
</tr>
<tr>
<td>Municipal sanitary</td>
<td>Water supply wells</td>
</tr>
<tr>
<td>Underground storage tanks</td>
<td>Other wells (non-waste)</td>
</tr>
<tr>
<td><strong>Category III - Sources designed to retain substances during transport or transmission</strong></td>
<td><strong>Category VI - Naturally occurring sources whose discharge is created and/or exacerbated by human activity</strong></td>
</tr>
<tr>
<td>Pipelines</td>
<td>Groundwater-surface water interactions</td>
</tr>
<tr>
<td>Hazardous waste</td>
<td>Natural leaching</td>
</tr>
<tr>
<td></td>
<td>Salt-water intrusion/brackish water up coning</td>
</tr>
</tbody>
</table>
Useful compilations on sources of groundwater contamination are discussed by Freeze and Cherry (1979), Pye et al. (1983), and Gordon (1984).

2.3 LANDFILL LEACHATE

One of the major constituents of sources of groundwater contamination is leachate through landfills. It has been explained in detail in the following paragraph. Leachate may be defined as a liquid that has percolated through solid waste and has extracted, dissolved or suspended materials. The large number of cases of groundwater pollution at landfills (Arneth et al. 1989) and the huge amount of money spent for remediation suggest that a landfill leachate is a significant source of groundwater pollution. Christensen et al. (1994) reviewed the information about the processes important in attenuation of landfill leachate plumes. Later, Christensen et al. (2001) updated the information about the composition and characteristics of leachates in different landfills. Apart from it, a large body of work on the chemical composition of landfill leachates can be found in Ehrig (1983, 1988), Andreottola and Cannas (1992), Tchobanoglous et al. (1993), Chu et al. (1994), Robinson (1995), Owen and Manning (1997), Krug and Ham (1997), Vadillo et al. (1999), Kjeldsen et al. (2002), Jorstad et al. (2004), Aghamohammadi et al. (2007), Renou et al. (2008) and Oygard (2009). Landfill leachate is generated by excess rainwater percolating through the waste layers. Combined physical, chemical and microbial processes in the waste transfer pollutants from the waste material to the percolating water (e.g. Christensen and Kjeldsen, 1989). Landfills receive mixture of municipal, commercial and mixed industrial waste, but excluding significant amounts of concentrated specific chemical waste. Table 2.3 shows typical compositional properties of leachates in landfills.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>pH</td>
<td>6.2-7.6</td>
<td>4.5-9</td>
<td>4.5-9</td>
<td>4.5-7.5</td>
<td>6.6-7.5</td>
<td>6.2-8.3</td>
<td>7.3-7.8</td>
</tr>
</tbody>
</table>

Constituent | Concentration (mg/l) |
---|---|
**Organic Carbon Constituent**<br>COD | 66-11600 | 500-60000 | 500-60000 | 3000-60000 | 100-500 | 460-40000 | 14900-19980 | 140-152000 |
BOD₅ | 2-8000 | 20-40000 | 20-40000 | 2000-30000 | 100-200 | 20-27000 | 6900-11000 | 20-57000 |
TOC | 21-4400 | 100-5000 | 1500-2000 | 80-160 | 150-1200 | 4550-6000 | 30-29000 |
**Nitrogen Constituent**<br>Org.N | 0.9-160 | 10-4250 | -- | 10-800 | 80-120 | -- | -- | 14-2500 |
NH₃-N | 5-730 | 30-3000 | 30-3000 | 10-800 | 20-40 | -- | 1120-2580 | 50-2200 |
**Anions**<br>Cl⁻ | 43-2800 | 100-5000 | -- | 200-3000 | 100-400 | 315-12400 | 5620-6330 | 150-44500 |
PO₄³⁻ | 0.02-4.4 | ---- | - | 5-100 | 5-10 | - | -- | 0.1-23 |
SO₄²⁻ | 55-460 | 10-1750 | 10-1750 | 50-1000 | 20-50 | 20-2500 | 142-352 | 8-7750 |
**Metals**<br>Na | 43-2500 | 50-4000 | - | 200-2500 | 100-200 | 1-6800 | - | 70-7700 |
Mg | 12-480 | 40-1150 | - | 50-1500 | 50-200 | 25-600 | 363.8-640 | 30-15000 |
K | 20-650 | 10-2500 | - | 200-1000 | 100-200 | 170-1750 | -- | 50-3700 |
Ca | 130-1200 | 10-2500 | 10-2500 | 200-3000 | 100-400 | 49-2300 | 97-787.5 | 10-7200 |
**Heavy Metals** | | | | | | | | |
Mn | 0.19-26 | 0.03-60 | - | - | - | -- | 0.11-5.3 | 0.03-1400 |
Fe | 0.09-380 | 3-2100 | 3-2100 | 50-1200 | 20-2000 | 2-500 | 14.2-44 | 3.5-5000 |
Cr | 0.005-0.14 | 0.03-1.6 | 30-1600 | - | - | 0.002-0.53 | 0.02-0.78 | 0.02-1.5 |
Ni | 0.02-0.16 | 0.02-2.05 | 20-2050 | - | - | 0.01-0.1 | 0.32-0.45 | 0.015-13 |
Cu | 0.004-0.15 | 0.04-1.4 | 4-1400 | - | - | 0.05-0.56 | 0.02-0.13 | 0.005-10 |
Zn | 0.02-0.95 | 0.03-120 | 0.03-120 | - | - | 0.05-16 | 0.38-1.06 | 0.03-1000 |
Cd | 0.002-0.13 | 0.0005-0.14 | 0.5-140 | - | - | 0.0007-0.525 | 0.01 | 0.0001-0.4 |
Pb | 0.003-0.22 | 0.008-1.02 | 8-1020 | - | - | 0.008-0.4 | 0.04 | 0.001-5 |

### 2.3.1 LANDFILL LEACHATE POLLUTANTS

Landfill leachates may be characterized as water-based solutions of four groups of pollutants (Christensen et al. 1994). The four groups of pollutants are

i) dissolved organic matter

ii) inorganic macro components
iii) heavy metals
iv) xenobiotic organic compounds (XOC)

Other compounds are also found in leachates from landfills such as B, As, Se, Ba, Li, Hg and Co. These compounds are generally low in concentrations. Leachate composition varies significantly among landfills depending upon waste composition, waste age and landfill technology. Leachate sampling methods and sample handling routines may also influence the measured leachate quality.

Each of the above pollutants is explained in the following:

2.3.1.1 Dissolved Organic Matter

It is a bulk parameter covering a wide range of very small volatile acids to fulvic and humic acid (Chian and DeWalle, 1977). There is not much information available on the composition of dissolved organic matter. Harmsen (1983) analysed both acid-phase leachate and methanogenic-phase leachate. In acid-phase leachate, 95% of dissolved organic content contains 20,000 mg/l of volatile fatty acids and only 1.3% of the dissolved organic content consists of compounds of high molecular weight. Apart from this, it has volatile amines and alcohols in a few percentage. In methanogenic-phase leachate, 32% of dissolved organic content has compounds of high molecular weight. Artiola-Fortuny and Fuller (1982) analysed methanogenic phase leachate and found that 60% of the dissolved organic content has humic material. Frimmel and Weis (1991) investigated anaerobic and aerobic leachates and found that only 6%-30% of the dissolved organic content has fulvic acid. Weis et al. (1989) compared fulvic acids from landfill leachates with those from soil and bog lake water. The fulvic acids isolated from landfill leachates has higher C, H and S content, lower quantities of phenolic groups, lower complexation capacities for Cu and lower molecular weight. Christensen et al. (1998a) characterized 82% of the dissolved organic content in leachate-polluted groundwater sampled less than 10 m down gradient from the Vejen Lanfill (DK) and found 49% fulvic acids, 8% humic acids and 25% hydrophilic fraction.

2.3.1.2 Inorganic macrocomponents

The concentrations of inorganic macrocomponents mainly depend upon stabilization of landfills. Ca, Mg, Fe and Mn are in the lowest concentrations in
methogenic phase. This is due to higher pH which enhances precipitation and sorption. Sulphate concentration is the lowest in the methanogenic phase due to microbial reduction of $\text{SO}_4^{2-}$ to $\text{S}^{2-}$. The other macro-components such as $\text{Cl}^-$, $\text{Na}$, and $\text{K}$ concentration in the landfill leachate are not influenced by precipitation, complexation and sorption. Decreasing trends in concentration of these pollutants with time could be due to wash-out by leaching. But Ehrig (1983, 1988) did not observe any decreasing trend in concentration of these parameters. Ehrig (1983, 1988) performed a detailed study on leachates from a large number of landfills in Germany. Similar findings are presented in a study on 13 sanitary landfills in Wisconsin USA (Krug and Ham, 1977), where equivalent concentration ranges and time dependency parameters were found. Ammonia was in the range of 500-2000 mg/l in most of the landfill leachates. There is no decreasing trend in the concentration of ammonia with time. Ammonia is released from the waste mainly by decomposition of proteins.

2.3.1.3 Heavy metals

In general, concentrations of heavy metals in leachates from different landfills (see Table 2.3) show major variations. On average, the concentrations of heavy metals in landfill leachates is low. Kjeldsen and Christopher, 2000 conducted a survey of 106 old Danish landfills and concluded that heavy metal concentration in the leachates is low. They estimated that there are 0.006 mg Cd/l, 0.13 mg Ni/l, 0.67 mg Zn/l, 0.07 mg Cu/l, 0.07 mg Pb/l and 0.08 mg Cr/l. Metals like Hg and Co are rare in leachates. Several investigations revealed Cd species in landfill leachate. It was observed (Lun and Christopher, 1989; Bolton and Evans, 1991 and Holm et al. 1995b) that free divalent $\text{Cd}^{2+}$ species in landfill leachates make up only a small part in Cd species. Heavy metals are usually associated with colloid content in leachates (Jensen and Christensen, 1999; Gounaris et al. 1993). In all these investigations, a comparison of the distribution of organic matter and heavy metals between the size fractions indicated that heavy metals in the colloidal fractions were not simply related to organic matter, even though colloidal humic substances are suspected to play a major role with respect to the speciation of the heavy metals.
2.3.1.4 Xenobiotic organic compounds (XOCs)

Table 2.3 presents concentration ranges of the most frequently found Xenobiotic compounds in landfill leachates. The most frequently found XOCs in landfill leachates are aromatic hydrocarbons (benzene, toluene, ethylbenzene and xylene) and halogenated hydrocarbons like tetrachloroethylene and trichloroethylene. These pollutants are available in high concentrations. Phenoxyalkanoic acid herbicides are newly identified compounds (Schulz and Kjeldsen, 1986; Gintanus et al. 1992, Kjeldsen 1993; Oman and Hynning, 1993). The concentration of XOCs in landfill leachates is expected to decrease over time, depending for each compound on its degradation in the landfill and its volatilaztion with the landfill gas (Kjeldsen and Christensen, 2000). Ravi et al. (1998) found highly varying concentration of Cl\(^{-}\) benzene and 1, 1-DCA just downgradient from the west KL landfill (USA) for a 15 a period (see Fig 2.1).

![Figure 2.1](image)

Fig 2.1 Temporal variations (15a) in leachate quality monitored in two wells (Ravi et al. 1988).
2.4 CONTAMINANT TRANSPORT AND FATE

Another important aspect of groundwater contamination is contaminant transport and fate. It is very important to understand various processes that affect transport (migration) and fate (chemical form and concentration).

The major processes affecting the contaminants in subsurface can be grouped in the following three categories:

1. Transport processes: Include advection, diffusion and dispersion;
2. Chemical mass transfer processes: Include sorption and desorption, dissolution and precipitation, oxidation and reduction, acid-base reaction, complexation, ion exchange volatilization and hydrolysis and
3. Biological process (or biodegradation)

The following paragraphs discuss the above processes.

2.4.1. ADVECTION

Advection, also known as advective transport or convection, refers to the contaminant movement by flowing water in response to a hydraulic gradient. The direction of hydraulic gradient dictates to a large extent the direction of dissolved contaminant transport. If advection is the only mechanism of transport the pore velocity (Darcy’s velocity divided by porosity) is an indicator of the transport of dissolved contaminants. The groundwater velocity for one dimensional steady-state flow is given by Darcy’s law as

\[ v = k i \]  \hspace{1cm} (2.1)

where \( v \) is the discharge velocity or Darcy’s velocity, \( k \) is the hydraulic conductivity and \( i \) is the hydraulic gradient. The seepage or actual velocity \( (v_s) \) is calculated using

\[ v_s = k i / n_e \] \hspace{1cm} (2.2)

where \( n_e \) is the effective porosity. Under one-dimensional steady state flow condition, the contaminant mass flux (i.e mass per unit area per unit time) due to advection is given by

\[ F_v = v C = n_e v_s C \] \hspace{1cm} (2.3)

where \( C \) is the dissolved contaminant concentration. Under uniform flow conditions, the advective transport is described by
\[
\frac{dC}{dt} = -v_s \frac{dC}{dx}
\]  

(2.4)

The solution to this equation implies that, if a contaminant of concentration \(C_0\) is introduced in the flowing groundwater, it will be transported in time \(t\), a distance \(x = v_s t\) as a plug, due to advection. Advection model helps to predict the fate of ground water contamination. To determine the factors controlling transport of nitrate-N into the Mississippi River Valley alluvial aquifer, a study was conducted during 2006 to 2008 to estimate fluxes of water and solutes for a site in the Bogue Phalia basin (1,250 km\(^2\)). Water-quality data were collected from a shallow water-table well, a vertical profile of temporary sampling points, and a nearby irrigation well. Nitrate was detected within 4.4 m of the water table but was absent in deeper waters with the evidence of reducing conditions and denitrification. Recharge estimates from 6.2 to 10.9 cm/year were quantified using water-table fluctuations, a Cl\(^-\) tracer method, and atmospheric age-tracers. A mathematical advection-reaction model predicted similar recharge to the aquifer, and also predicted that 15% of applied nitrogen is leached into the saturated zone. (Welch et al. 2011).

2.4.2 DIFFUSION

Diffusion, which is molecular diffusion, refers to the movement of contaminants under a chemical concentration gradient (i.e. from an area of greater concentration toward an area of lower concentration). Diffusion can occur even when the fluid is not flowing or is flowing in the direction opposite to contaminant movement. Diffusion is characterized using Fick’s first law. For one-dimensional conditions, this law can be expressed as

\[
F_d = -D^* \frac{dC}{dx}
\]  

(2.5)

Where \(F_d\) is the diffusive mass flux per unit area per unit time, \(D^*\) is the effective diffusion coefficient and \(\frac{dC}{dx}\) is the concentration gradient. The values of \(D^*\) do not vary significantly for different soils and contaminant combinations. They range from \(1 \times 10^{-9}\) to \(2 \times 10^{-9}\) m\(^2\)/s (Mitchell, 1976). The \(D^*\) in the equation also accounts for tortuosity in the soils and can be related to self diffusion coefficients (\(D_0\)) of chemicals as follows

\[
D^* = \tau D_0
\]  

(2.6)
where τ the tortuosity coefficient which has a value less than 1. The $D_0$ values for selected chemicals are shown in Table 2.4. The values of τ range from 0.01 and 0.5 (Freeze and Cherry, 1979). The values of τ (or $D^*$) can be determined by laboratory tests using the steady-state method, time lag method, and transient method. The transient method is subdivided into the column method and the half-cell method. A description of these test methods and the determination of $D^*$ are given by Rowe et al. (1988), Shackelford and Daniel (1991b), and Sharma and Lewis (1994).

Table 2.4 Self diffusion coefficients ($D_0$) for ions at infinite dilution in water (Source: Sharma and Lewis, 1994; Fetter, 1999)

<table>
<thead>
<tr>
<th>Chemical</th>
<th>$D_0 \times 10^{-10}$ (m²/s)</th>
<th>Chemicals</th>
<th>$D_0 \times 10^{-10}$ (m²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Anions</td>
<td>Cations</td>
<td></td>
</tr>
<tr>
<td>OH$^-$</td>
<td>52.8</td>
<td>H$^+$</td>
<td>93.1</td>
</tr>
<tr>
<td>F$^-$</td>
<td>14.7</td>
<td>Li$^+$</td>
<td>10.3</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>20.3</td>
<td>Na$^+$</td>
<td>13.3</td>
</tr>
<tr>
<td>Br$^-$</td>
<td>20.8</td>
<td>K$^+$</td>
<td>19.6</td>
</tr>
<tr>
<td>I$^-$</td>
<td>20.4</td>
<td>Rb$^+$</td>
<td>20.7</td>
</tr>
<tr>
<td>HCO$_3^-$</td>
<td>11.8</td>
<td>Cs$^+$</td>
<td>20.5</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>19</td>
<td>Be$^{2+}$</td>
<td>5.98</td>
</tr>
<tr>
<td>SO$_4^{2-}$</td>
<td>10.6</td>
<td>Mg$^{2+}$</td>
<td>7.05</td>
</tr>
<tr>
<td>CO$_3^{2-}$</td>
<td>9.22</td>
<td>Ca$^{2+}$</td>
<td>7.92</td>
</tr>
<tr>
<td></td>
<td>Organics</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Acetone</td>
<td>10.24</td>
<td>Pb$^{2+}$</td>
<td>9.25</td>
</tr>
<tr>
<td>N-Butyl alchol</td>
<td>8.98</td>
<td>Cu$^{2+}$</td>
<td>7.13</td>
</tr>
<tr>
<td>Chlorobenzene</td>
<td>8.42</td>
<td>Fe$^{2+}$</td>
<td>7.19</td>
</tr>
<tr>
<td>Ethylbenzene</td>
<td>7.54</td>
<td>Cd$^{2+}$</td>
<td>7.17</td>
</tr>
<tr>
<td>Tetrachloroethylene</td>
<td>8.4</td>
<td>Zn$^{2+}$</td>
<td>7.02</td>
</tr>
<tr>
<td>Methyl alchol</td>
<td>14.65</td>
<td>Ni$^{2+}$</td>
<td>6.79</td>
</tr>
<tr>
<td>1,1,1-Trichloroethane</td>
<td>8.53</td>
<td>Fe$^{3+}$</td>
<td>6.07</td>
</tr>
<tr>
<td>Trichloroethane</td>
<td>9.89</td>
<td>C$^{3+}$</td>
<td>5.94</td>
</tr>
<tr>
<td>Carbon disulfide</td>
<td>11.53</td>
<td>Al$^{3+}$</td>
<td>5.95</td>
</tr>
</tbody>
</table>

Similar data can be found in Li and Gregory, (1974), Lerman (1979), and Quigley et al. (1987). The values of $D_0$ reported in Table 2.5 should be considered to be the
maximum values attainable under ideal conditions (i.e molecular scale, infinite dilution). Under conditions which are not ideal (e.g macroscopic scale, concentrated solutions), a number of effects negligible for ideal conditions, become important. (Schakelford 1991a). For example, when two oppositely charged ions are diffusing in solution, an electric potential gradient, the slower moving ions speed up while the faster moving ions slow down, the overall result being that both ions migrate at the same speed. This electric potential effect is responsible, in part, for the differences between simple electrolyte diffusion values shown in Table 2.5 and their respective self diffusion coefficients are given in Table 2.4. Other effects responsible for the differences in $D_0$ values under non ideal conditions include solute-solute and solute-solvent interactions (Robinson-Stokes, 1959).

Table 2.5 Limiting free-solution diffusion coefficients for representative simple electrolytes at 250 C [modified Robinson and Stokes (1959)]

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>$D_0 \times 10^{10}$ (m$^2$/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HCl</td>
<td>33.36</td>
</tr>
<tr>
<td>HBr</td>
<td>34.00</td>
</tr>
<tr>
<td>LiCl</td>
<td>13.66</td>
</tr>
<tr>
<td>LiBr</td>
<td>13.77</td>
</tr>
<tr>
<td>NaCl</td>
<td>16.10</td>
</tr>
<tr>
<td>NaBr</td>
<td>16.25</td>
</tr>
<tr>
<td>NaI</td>
<td>16.14</td>
</tr>
<tr>
<td>KCl</td>
<td>19.93</td>
</tr>
<tr>
<td>KBr</td>
<td>20.16</td>
</tr>
<tr>
<td>KI</td>
<td>19.99</td>
</tr>
<tr>
<td>CsCl</td>
<td>20.44</td>
</tr>
<tr>
<td>CaCl$_2$</td>
<td>13.35</td>
</tr>
<tr>
<td>BaCl$_2$</td>
<td>13.85</td>
</tr>
</tbody>
</table>
The value of $D_0$ also depends on the type of diffusion. There are essentially four different types of diffusion (Robinson and Stokes, 1959; Li and Gregory, 1974; Lerman 1979; Shackelford 1989): 1) Self-diffusion 2) tracer diffusion 3) salt diffusion and 4) counter diffusion or inter diffusion. Figure 2.2 shows different types of diffusion.

![Diffusion Cells](image)

**Fig 2.2** Diffusion cells for different diffusion system a) Self-diffusion; b) Tracer diffusion c) Salt-diffusion; d) Counterdiffusion [after Shackelford (1988)]

From Fick’s first law and the equation of continuity, the rate at which contaminants diffuse in soils can be given by

$$\frac{dC}{dt} = D^* \frac{d^2C}{dx^2}$$

(2.7)
This is known as Fick’s second law. For the initial condition, \( C(x,0) = 0 \) (assuming that the porous medium is initially contaminant free) and boundary conditions \( C(0,t) = C_0 \) and \( C(\alpha,0) = 0 \), the solution to this equation is given by (Crank, 1956) as

\[
C(x,t) = C_0 \text{ erfc} \left( \frac{x}{2\sqrt{D't}} \right)
\]  

(2.8)

2.4.3 DISPERSION:

Dispersion of waste contaminants in an aquifer causes the concentration of contaminants to decrease with increasing length of flow (U.S. Environmental Protection Agency, 1985). Dispersion is caused by: (1) molecular diffusion (important only at very low velocities) and (2) hydrodynamic mixing (occurring at higher velocities in laminar flow through porous media). Contaminants traveling through porous media have different velocities and flow paths with different lengths. Contaminants moving along a shorter flow path or at a higher velocity, therefore, arrive at a specific point sooner than contaminants following a longer path or traveling at a lower velocity, resulting in hydrodynamic dispersion. Figure 2.3 shows that dispersion can occur in both longitudinal (in the direction of ground-water flow) and transverse (perpendicular to ground-water flow) directions, resulting in the formation of a conic waste plume downstream from a continuous pollution source (U.S. Environmental Protection Agency, 1985).

Fig 2.3 The Effects of Ground-Water Velocity on Plume Shape. Upper Plume Velocity: 1.5 ft/day and Lower Plume Velocity: 0.5 ft/day (US Environmental Protection Agency, 1985).
The concentration of waste contaminants is less at the margins of the plume and increases towards the source. A plume will increase in size with more rapid flow within a time period, because dispersion is directly related to ground-water velocity.

The dispersion coefficient varies with ground-water velocity. At low velocity, the dispersion coefficient is relatively constant, but increases linearly with velocity as ground-water velocity increases. Based on these observations, investigators proposed that the dispersion coefficient can be expressed as the sum of an effective molecular diffusion coefficient and a mechanical dispersion coefficient (Palmer and Johnson, 1989a). The effective molecular diffusion coefficient is a function of the solution diffusion coefficient and the tortuosity of the medium. Tortuosity accounts for the increased distance a diffusing ion must travel around sand grains. The mechanical dispersion coefficient is proportional to velocity. Specifically, mechanical dispersion is a result of: (1) velocity variations within a pore, (2) different pore geometries, and (3) divergence of flow lines around sand grains present in a porous medium (Gillham and Cherry, 1982).

2.5 CONTROL OF CONTAMINANT TRANSPORT THROUGH LINERS

As it has been discussed earlier, the leachates generated from landfill wastes is considered as a primary source of groundwater contamination. The water leaches from the landfill collecting contaminants in the wastes by physical, chemical and microbial processes and percolates deep into the layers of soil, causing groundwater pollution (Kelly, 1976). The impact of waste disposal facility on groundwater quality depends on the nature of the site, the initial conditions of the soil, the type of waste, the local hydrogeology, the presence of a dominant flow path, and most importantly, the nature of the barrier that is intended to limit and control contaminant migration. Soil liners are used as barriers to prevent the migration of pollutants into natural resources such as groundwater.

In engineering practice, naturally available clay is compacted in a single or multiple layers to serve the function of a soil liner. Natural clays or other fine-grained soils are preferred as soil liners because of their ability to impede the flow of water due to their low hydraulic conductivity. They are also capable to adsorb several contaminants. Fine-grained clayey soils are preferred because of their availability at a relatively low
cost. In addition, positive and extensive experience of using fine-grained clayey soils in several geotechnical structures such as earth dams for several decades has encouraged the use of fine-grained soils as materials for soil liners. The first liners used in engineering practice consisted of a single compacted clay liner without providing a leachate collection system. However, more recent soil liners have leachate collection systems incorporated in their design. The most common liner system consists of a clay liner overlain by a sand layer. The thickness of the clay liner can vary from location to location, and the nature of the project depending on the soil properties, from as thin as 0.15 m to as thick as 4 m (Benson, 2000). One of the key properties to be ensured is the hydraulic conductivity value of the compacted soil liner. Benson et al. (1994) suggest ranges for various soil properties such as the Atterberg limits, the plasticity index, and the percentage of fines which will result in a hydraulic conductivity value lower than 1 x 10^{-7} cm/sec. These suggestions were provided after analyzing 67 landfills in North America. Different types of liner systems have been developed recently in order to reduce the environmental impact caused by leachate into the aquifers. They are compacted clay liners, geosynthetic clay liners, composite liners, fly ash liners, lateritic soils etc.

2.5.1 COMPACTED CLAY LINERS

Compacted clay liners (CCLs), are the oldest engineered component used in landfills and have been employed for many years as engineered hydraulic barriers for waste-containment facilities (Daniel and Koerner, 1995). Compacted natural clays are widely used as liners due to their high contaminant attenuation and cost effectiveness (attributed to easy availability and low transportation cost). According to the United States Environmental Protection Agency (USEPA), compacted soil liners must be at least approximately 60 cm thick and must have a hydraulic conductivity of no more than 1 x 10^{-7} cm/sec. To meet this requirement certain characteristics of soil material should be met (Qian et al. 2002). First, the soils should contain at least 15-20 % of silt or clay-sized material. Secondly, the plasticity index should be greater than 10%. Soils with very high PI, greater than 30 to 40 percent, are sticky and are difficult to work with. Also, high PI soils form hard clumps when the soils are dry and difficult to break during compaction. Thirdly, the coarser fragments should be screened to not more than 10% gravel-size particles. Soils with greater percentages of coarser fraction can contain zones of gravel
which will have high hydraulic conductivity. Finally, the material should contain soil particles or chunks of rock larger than 1 to 2 inches in diameter, which may form a permeable window through a layer. Thus, the specifications for clay liners (Rowe et al.1995), often include:

a) A minimum cation exchange capacity of 10 meq/100 g of soil;

b) Compaction or cementation to high densities and effective porosities that are low enough to minimize the flow of contaminants through them; the maximum hydraulic conductivity allowable is about $10^{-7}$ cm/s;

c) Compatibility with the leachates to be contained; the liner should be compatible with the leachates to be retained, such that the hydraulic conductivity shall not increase significantly on exposure to leachate;

d) A chemical flux point of $10^{-8}$ cm/s or less is preferable since the diffusion often becomes the dominant migration mechanism; and

e) It should plug the pore space in natural soil such that large channels for contaminant transport are effectively eliminated.

Bentonite clay based materials are preferred because of their low hydraulic conductivity and good adsorption or retention capacity (Daniel, 1993: Rowe et al. 1995). Also, high plastic bentonite–based clays are extremely difficult to work with in the field. These materials maintain their low hydraulic conductivity and diffusivity for a longer period of time under a different environmental condition (Oscarson et al.1996).

2.5.2 GEOSYNTHETIC CLAY LINERS

Geosynthetic clay liners (GCLs) represent a relatively new technology (developed in 1986) currently gaining acceptance as a barrier system in municipal solid waste landfill applications. A GCL is a relatively thin layer of processed clay (typically bentonite) either bonded to a geomembrane or fixed between two sheets of geotextiles. A geomembrane is a polymeric sheet material that is impervious to liquid as long as it maintains its integrity. A geotextile is a woven or nonwoven sheet material less impervious to liquids than a geomembrane, but more resistant to penetration damage. Both types of GCLs are illustrated in Figure 2.4. Although the overall configuration of a GCL affects its performance characteristics, the primary performance factors are clay quality, amount of clay used per unit area and uniformity. Bentonite is extremely...
absorbent, granular clay formed from volcanic ash. Bentonite attracts positively charged water particles; thus, it rapidly hydrates when exposed to liquids, such as water or leachate. As the clay hydrates it swells, giving it the ability to “self-heal” holes in the GCL. Laboratory tests on bentonite revealed that a hole up to 75 millimeters in diameter will seal itself, allowing the GCL to retain the properties that make it an effective barrier system. The US EPA considers GCLs as an auxiliary application to enhance the performance of engineered landfills and also as a substitute for CCLs (Carson, 1995).

Bentonite sandwiched between two geotextile

Bentonite glued to geomembrane

Fig 2.4 General configuration of a GCL (U.S. EPA, 2001)

GCLs are used in a wide variety of environmental lining applications such as decorative ponds, secondary containment structures, waste lagoons, water canals, heap leach ponds and landfill bottoms and caps. They are considered as replacements for compacted clay liners (CCLs) or as supplements to CCL based composite liner systems. GCL technology offers some unique advantages over conventional bottom liners and covers. GCLs, for example, are fast and easy to install, have low hydraulic conductivity and have the ability to self repair any rips or holes caused by the swelling properties of
bentonite from which they are made. GCLs are cost effective in regions where clay is not readily available (Trauger and Tewes, 1995). Table 2.6 gives a detailed comparison of geosynthetic clay liners and compacted liners as elaborated by Daniel (1993).

Table 2.6 Comparison of geosynthetic clay liners and compacted clay liners (after Daniel, 1993)

<table>
<thead>
<tr>
<th>Characteristic</th>
<th>Geosynthetic clay liners</th>
<th>Compacted clay liners</th>
</tr>
</thead>
<tbody>
<tr>
<td>Materials</td>
<td>Bentonite, adhesives geotextiles and Geomembranes</td>
<td>Native soils or blend of soil and bentonite</td>
</tr>
<tr>
<td>Thickness</td>
<td>Approximately 12 mm; consumes very little landfill volume</td>
<td>Typically 300 to 600 mm; consumes more landfill volume</td>
</tr>
<tr>
<td>Hydraulic conductivity</td>
<td>( \leq 1 \text{ to } 5 \times 10^{-9} \text{ cm/s} )</td>
<td>( \leq 1 \times 10^{-7} \text{ cm/s} )</td>
</tr>
<tr>
<td>Speed and ease of construction</td>
<td>Rapid and simple installation</td>
<td>Slow and complicated construction</td>
</tr>
<tr>
<td>Vulnerability to damage during construction from desiccation and freeze-thaw</td>
<td>GCLs are essentially dry; GCLs cannot desiccate during construction; not particularly vulnerable to damage from freeze-thaw</td>
<td>Compacted clay liners are nearly saturated; can desiccate during construction; vulnerable to damage freeze-thaw.</td>
</tr>
<tr>
<td>Vulnerability to damage from differential settlement</td>
<td>Can withstand much greater differential settlement than compacted clay liner</td>
<td>Cannot withstand much differential settlement without cracking</td>
</tr>
<tr>
<td>Availability of materials of</td>
<td>Materials easily shipped to any site</td>
<td>Suitable materials not available at all sites</td>
</tr>
<tr>
<td>Cost</td>
<td>Reasonably low, highly predictable cost that does not vary much from project to project</td>
<td>Highly variable-depends greatly on characteristics of locally soils</td>
</tr>
<tr>
<td>Ease of repair</td>
<td>Ease of repair with patch place over problem area</td>
<td>Very difficult to repair, must mobilize heavy earth-moving equipment if large area requires repair</td>
</tr>
<tr>
<td>Experience</td>
<td>Limited to novelty</td>
<td>Has been used for many years</td>
</tr>
<tr>
<td>Regulatory approval</td>
<td>Equivalence in meeting performance objects</td>
<td>Compacted clay liners are usually required by regulatory</td>
</tr>
<tr>
<td>Construction</td>
<td>Manufactured in factory and installed in field.</td>
<td>Constructed entirely in field</td>
</tr>
<tr>
<td>Installation equipment</td>
<td>Light installation equipment</td>
<td>Heavy installation equipment</td>
</tr>
<tr>
<td>Fissures</td>
<td>Cannot develop fissures if moisture available</td>
<td>May develop fissures</td>
</tr>
<tr>
<td>Weight</td>
<td>Light weight</td>
<td>Large weight</td>
</tr>
</tbody>
</table>
Despite these advantages of GCLs, the currently available GCLs have the following limitations:

i) It is generally seen that the bentonite powder may start coming out of the GCL during either transportation or placement. This could be more severe, where woven fabric is used as a carrier, or in the case of nonwoven, it is too thin a fabric.

ii) During transportation and handling of GCLs the bentonite powder or granules is no more uniformly distributed. This may become worse during placement.

iii) There is a possibility of geosynthetic component being degraded in the long term. According to Giroud (1996) some fungi and bacteria may catalyse hydrolysis of polysters.

iv) Limited sorption capacity

Advantages and disadvantages of GCL are briefly discussed by Bouzza (1997) and Bouzza (2002).

### 2.5.3 COMPOSITE LINERS

A composite liner is a liner that consists of two or more components. In most cases where a composite liner is used in a landfill, the composite liner consists of a geomembrane and a low-permeability soil layer. Typically, the geomembrane component of the composite liner is placed on top of the low-permeability soil layer, which decreases percolation of leachate into the liner and promotes lateral flow of leachate in the leachate collection layer overlying the composite liner since the geomembrane is less permeable than the low-permeability soil (Figure 2.5). In otherwords, leachate collection and removal is maximized and percolation of leachate into the liner is minimized.

![Fig 2.5 Leachate flow in the leachate collection layer overlying composite liner (source: Giroud et al. 1997)](image)
In the current state of practice for landfill design, the low-permeability soil component of composite liners is either a CCL or a GCL. CCLs are typically 0.3 to 1.5 m thick and are constructed in lifts approximately 0.15 m thick after compaction. GCLs are on the order of 5 to 10 mm thick and consist of a thin layer of clay soil associated with one or two geosynthetic layers. CCLs or GCLs are used in composite liners because of low permeability. The hydraulic conductivities of GCLs and CCLs vary depending on the compressive stress. The measured hydraulic conductivities of hydrated GCLs in laboratory tests designed to simulate the compressive stress conditions in a landfill are typically in the range of $5 \times 10^{-12}$ m/s to $5 \times 10^{-11}$ m/s. These hydraulic conductivities are roughly 10 to 100 times lower than the hydraulic conductivities of CCLs which are typically between $1 \times 10^{-10}$ m/s and $1 \times 10^{-9}$ m/s. The physical characteristics and engineering properties of commercially-available GCL products are described by Daniel and Boardman (1993). The hydraulic conductivity values given above are for the cases when the liquid permeating the CCL or the GCL is water or a low-concentration leachate that does not affect the hydraulic conductivity of the CCL or the GCL. Examples of such leachates are given by Ruhl and Daniel (1997). Fig 2.6 shows the types of composite liners.
Fig 2.6 Examples of composite liners in (a) Single liner systems; (b) Double liner systems; and (c) Cover systems (modified after Daniel and Koerner, 1995)
2.5.4. FLY ASH LINERS

Either in CCL or GCL or composite liner clays play a significant role in reducing leachate migration through its low permeability. However bentonite clay undergoes large differential settlements, which may reduce the effectiveness of leachate collection system. Moreover, the properties of bentonite clay liners can alter due to leachate mineral interactions and increase leakage rate to the above design (Elsbury et al. 1990). Alternatively, the potential waste material “fly ash” is considered as a liner material. Coal fly ash is a waste produced through burning of coal in thermal power stations for the production of electricity. Fly ash particles, which are silt-sized, are non-plastic and do not possess surface charges. However, the unburned carbon present in fly ash helps to adsorb many ions present in the leachate (La Grega et al. 1994). High carbon fly ashes are particularly good for the organic contaminants in the leachate. Because of their alkalinity, fly ashes may precipitate most of the heavy metals present in the leachates. Many fly ashes are pozzolanic and develop good strength and acquire capacity to counter the effects of leachates (Bowders et al. 1987; Edil et al. 1987; McLaren and Digioia, 1987; Prashanth et al. 2001). Fly ashes generally posses greater hydraulic conductivity than clays (Bowders et al. 1990). However, the precipitates formed retard the migration of ions into the subsurface and ultimately into the groundwater. The precipitates can block the pores of the compacted fly ash, further reducing the hydraulic conductivity (Edil et al. 1992). Most metals precipitate at higher pH levels as hydroxides. The main disadvantage of using fly ash alone is that it has low cation exchange capacity and high hydraulic conductivity (Sivapullaiah and Lakshmikantha, 2004). The compressibility of fly ash reduces with alkaline solution but increases with acidic solution. So to improve the geotechnical properties of fly ash such as cation exchange capacity, shrinkage and volume change behaviour bentonite is added as an additive (Younus and Sreedeep, 2012).

2.5.5 COMPACTED LATERITIC SOIL LINERS

Liners and covers for municipal and hazardous waste containment facilities are often constructed with the use of fine-grained, low plasticity natural soils. When appropriately compacted, such fine-grained soils have low hydraulic conductivity and are capable of attenuating inorganic chemical species. Osinubi and Nwaaiwu (2002)
indicated that fine-grained lateritic soils can be used as hydraulic barrier layers for constructing waste containment structures in the absence of natural clay. Hydraulic conductivity of lateritic soils decreased with increase in dry unit weight and initial saturation, especially at higher fines content. Hydraulic conductivity values less than $1 \times 10^{-9}$ m/s can be obtained at dry unit weights (wet of optimum) and initial saturations greater than 16.0 kN/m$^3$ and 86%, respectively, provided minimum compaction energy equal to the British Standard Light effort is used. (Osinubi and Nwaiwu, 2005).

2.5.6 OTHER TYPES OF LINING MATERIAL

2.5.6.1 Soil cement liners:

Soil cement is a compacted mixture of Portland cement, water, and selected in-situ soils. The resulting mixture has greater strength than the natural soil. The hydraulic conductivity varies with particle size distribution of the soil. Fine textured soils (clays and clay loams) result in the lowest hydraulic conductivity with a range averaging near $10^{-8}$ m/sec to $10^{-9}$ m/sec. The addition of cement increases soil pH and forms less soluble compounds. The mechanism by which cement changes the properties of soil is explained by the formation of strong nuclei, distributed throughout the mass, or the formation of a skeleton of hydrated cement throughout the voids. For instance, montmorillonite clay supports, at low cement contents, a nucleated structure which changes to a skeleton structure as cement contents increase. The ageing and weathering characteristics of soil cement liner are good, especially those associated with wet-dry, and freeze-thaw cycles. Some degradation has been noted when soil cement is exposed to highly acidic environments. However, soil cement liners can resist moderate amounts of alkali, organic matter and inorganic salts. One of the main deficiencies of soil cement as a liner material is its tendency to crack and shrink on drying.

2.5.6.2 Soil carbonate liners:

Carbonates are some of the most common minerals in most rock types. The three major mineralized groups of carbonates are the calcite, aragonite and malachite groups, all of which include a range of carbonate minerals (Kraus et al.1959). The most widely known minerals are calcite and dolomite, both of which are from the calcite group. Mixing carbonates with soil may result in soil stabilization or cementations that
temporarily inhibit the movement of pollutants. Crushed carbonates vary in their degrees of effectiveness in minimizing migration of potential pollutants in aqueous leachate, depending on the way they are associated with the soil as well as the kind of soil involved. In leachate pollutant control, the purpose of carbonates is not necessarily to neutralize the acidity of soil, but to react directly with potentially toxic constituents of the leachate before they enter the soil as well as raise the pH level of the leachate. Fuller and Warrick (1985) have indicated that the use of carbonate liners over soil is preferred over other methods. Leachates high in acid, total organic carbon (TOC), and soluble salts possess a greater carbonate requirement than more dilute leachates (Alesii et al. 1980). Hence, fresh leachates consume carbonate more rapidly than older leachates. Consumption of carbonate is directly proportional to the leachate acidity. The greater the acidity, the greater the thickness of limestone required. This is due to the differences in the degree of dissolution. The most important properties that influence the way carbonates contribute to the effectiveness of liner systems are: (1) particle size distribution, (2) quality of the carbonate, (3) thickness of the carbonate layer, and (4) compaction.

2.5.6.3 Soil sealants liner

The hydraulic conductivity of some soils can be significantly reduced by the application of various chemicals or leachates. They may be water borne, mixed in place, spray applied, or injected below the soil surface (Gooding et al. 1967). Water-borne or spray-on polymer soil sealants can reduce hydraulic conductivity of earth-lined impoundments. However, the sealing effect is confined to the upper few centimeters and can be significantly diminished by the effects of wet-dry and/or freeze-thaw cycles. Types of sealants include resinous polymer, diesel fuel mixtures, petroleum-based emulsions, powdered polymers which form gels, and monovalent cationic salts. Soil sealants utilizing monovalent cations, such as sodium carbonate, sodium pyrophosphate and sodium silicate, chemically reduce the effective porosity of the soil due to the high tendency to form dispersed structure. Soil treated with sodium silicate and sulfuric acid prior to compaction shows a significant seepage reduction and is compatible with sulfuric acid-bearing wastes (Clark and Moyer, 1974). Soil sealants based on polymers are generally mixtures of linear and cross linked polymers of approximately the same
molecular weight. The linear portion sorbs to the soil, forming a flexible network. The cross linked polymer particles can flow, and thus conform to and permeate the soil pores. The polymer is usually mixed in a low pH water/acid solution and sprayed on an unfilled site as a low viscosity slurry. The low pH allows the slurry to penetrate the surface and form a deeper seal. The main disadvantages of polymer seals are: (1) low strength, and (2) exposure to salts, acids. Multivalent cations cause the polymers to shrink, increasing the hydraulic conductivity and decreasing the effectiveness of the seal (Parks and Rosene, 1971). For example, soil hydraulic conductivity to water decreased when latex was used as a soil sealant. However, the latex was subjected to damage by microbiological attack, frost action, and vegetation (Uniroyal, 1972).

2.5.6.4 Flexible membrane liners

Prefabricated liners based upon sheeting of polymeric materials are of particular interest for the lining of waste storage and disposal impoundments. As a group, these materials exhibit extremely low hydraulic conductivity. They have found substantial use in water impoundments in reservoirs and are being used in the lining of sanitary landfills and various waste disposal facilities. Types of flexible membrane liners include Polyvinyl chloride (PVC), Chloro-sulfonated Polyethylene (CSPE), Chlorinated Polyethylene (CPE), and Polyethylene.

Though many different types of liners exist, compacted clay liners (CCL) and geosynthetic clay liners (GCL) are predominantly used as hydraulic barriers because of their low hydraulic conductivity and high chemical compatibility to most solutions that come into contact with. The important characteristics of these liners such as hydraulic conductivity \( k \), chemical compatibility have been discussed below.

2.6 HYDRAULIC CONDUCTIVITY \( k \):

Low hydraulic conductivity \( k \) is a prime reason for choosing clay as a major component of waste containment barrier systems. It is well known that the hydraulic conductivity of clays can be strongly affected by the clay-fluid interaction (Mitchell, 1993). In the case of GCL, the hydraulic performance mainly depends upon the hydraulic performance of bentonite. Bentonite occurs as a product of weathering, through chemical
transformation from acid volcanic glass tufa (volcanic ashes), which has been deposited in sea water (Na-bentonite) or in fresh water (Ca-bentonite). High quality bentonite contains 65% to 95% montmorillonite mineral by weight (Egloffstein, 1997). A great number of experimental studies dealing with the effects of chemicals on hydraulic conductivity of GCLs and clays are available in the literature. Some of these studies focused on inorganic liquids (Daniel, 1993; Gleason et al. 1997; James et al. 1997; Petrov and Rowe, 1997; Petrov et al. 1997a; Lin and Benson, 2000; Shackelford et al. 2000; Egloffstein, 2001; Jo et al. 2001; Vasko et al. 2001; Jo et al. 2004; Kolstad et al. 2004a; Lee et al. 2005; Lee and Shackelford, 2005; Jo et al. 2005; Mishra et al. 2005; Yilmaz et al. 2008a, b). The other studies focused on organic liquids (Anderson et al. 1985; Foreman and Daniel, 1986; Bowders and Daniel 1987; Fernandez and Quigley, 1989; Kaya and Fang, 2000; Anandarajah, 2003; Park et al. 2006; Yong et al. 2007), and leachate components (Ruhl and Daniel, 1997; Kayabali and Mollamahmutoglu, 2000; Shan and Lai, 2002; Kolstad et al. 2004b). Most of the researchers pointed out that the hydraulic conductivity of high plasticity clays increased when the concentration of chemical solutions was increased. In some cases, interactions between the permeating liquid and the clay can result in significant increases (>10x) in the hydraulic conductivity of the clay relative to that based on water (Mitchell and Madsen, 1987; Shackelford, 1994; Shackelford et al. 2000). Most of the researchers were focused on the investigation of the hydraulic conductivity of higher activity clays such as bentonite or geosynthetic clay liners (GCL’s). Petrov and Rowe (1997) investigated how NaCl solutions of varying concentration affected the hydraulic conductivity of a GCL containing Na-bentonite. Tests were conducted with deionised water (DIW) and NaCl solutions having concentrations between 0.1-2.0 M. Hydraulic conductivity of the GCL increased as the NaCl concentration increased. At 2.0 M, the hydraulic conductivity was as much as 800 times higher than that with distilled water. Jo et al. (2001) investigated hydraulic conductivity and swelling of non-prehydrated GCLs permeated with single-species salt solutions such as LiCl, NaCl, KCl, CaCl2, MgCl2, ZnCl2, CuCl2 and LaCl3. Jo et al. (2005) conducted experimental tests to study long-term hydraulic conductivity of a geosynthetic clay liner permeated with some inorganic salt solutions (i.e. NaCl, KCl and CaCl2). Shackelford et al. (2000) studied the hydraulic conductivity of GCLs permeated
with nonstandard liquids such as NaCl, ZnCl₂ and CaCl₂. Lee et al. (2005) used CaCl₂ as the testing liquid for the determination of the hydraulic conductivity of geosynthetic clay liners. It was found out that the hydraulic conductivity of bentonite clay or GCLs increased when the concentration of salt solutions was increased.

Some researchers also compared the quality of clays on interaction with chemicals. Gleason et al. (1997) investigated some geotechnical properties of Ca and Na-bentonite with different concentrations of CaCl₂ (varying between 0.01 and 0.735 M), NaCl (varying between 0.01 and 0.1 M), and methanol (pure methanol and 50% methanol in distilled water), and gasoline. They reported that calcium bentonite would be more resistant than sodium bentonite to chemical constituents in the permeating fluids. Also, it was concluded that permeation with a strong calcium chloride solution would cause large increases in the hydraulic conductivity of sodium bentonite. Similarly, Stern and Shackelford (1998) investigated the substitution of attapulgite clay for bentonite in a sand-bentonite mixture on interaction with CaCl₂ solutions. They reported that for mixtures with the same clay soil content, complete substitution of attapulgite clay for bentonite significantly decreased the change in hydraulic conductivity relative to that observed for the sand-bentonite mixtures upon permeation with a 0.5M CaCl₂ solution. Another similar study was conducted by Lee and Shackelford (2005). They studied the impact of bentonite quality on the hydraulic conductivity of geosynthetic clay liners. They observed that the hydraulic conductivity for high-quality bentonite (k_H) is lower than the hydraulic conductivity for low quality bentonite (k_L), when specimens are permeated with water. However, k_H is always higher than that for k_L when the specimens are permeated with the CaCl₂ solutions. Thus, the GCL with the higher-quality bentonite is more susceptible to chemical attack than the GCL with lower-quality bentonite.

### 2.7 CHEMICAL COMPATIBILITY

The performance of earthen hydraulic barriers depends to a great extent on the hydraulic conductivity of the soil to the liquid being contained. Consequently, hydraulic conductivity tests are often conducted on the soil barrier material using the actual liquid to be contained or a liquid with representative properties. Such tests are often referred to as compatibility tests, because the primary objective of these tests is to determine whether
or not the barrier soil and permeant liquid are compatible, i.e., permeation with the liquid causes no significant change in hydraulic conductivity (Bowders et al. 1986; Bowders and Daniel 1987; Shackelford 1994; Shackelford et al. 2000). The results of several studies have shown the need to perform compatibility tests until the effluent and influent have the same chemical composition to ensure that all possible interactions between the permeating liquid and the soil have occurred (e.g. Shackelford 1994; Shackelford et al. 2000; Jo et al. 2005).

An alternative approach that is more rapid and less expensive and yet qualitative is to evaluate how index properties of the barrier soil (e.g. Atterberg limits, particle size, etc.) change when the liquid to be contained is used as the hydrating liquid during index testing. The underlying premise of these tests, which are referred to herein as surrogate compatibility tests, is that physicochemical changes that alter index properties also cause a change in hydraulic conductivity. (Dunn and Mitchell 1984; Bowders 1985; Bowders et al. 1986; Bowders and Daniel 1987; Daniel et al. 1988; Acar and Olivieri 1989; Shackelford 1994; Narejo and Memon 1995; Shackelford et al. 2000; Jo et al. 2001).

Liquid limit ($LL$) tests have been used by several investigators as surrogate compatibility tests (Bowders et al. 1986; Sridharan et al. 1986; Bowders and Daniel 1987; Daniel et al. 1988; Acar and Olivieri 1989; Edil et al. 1991; Shackelford 1994; Gleason et al. 1997; Petrov and Rowe 1997; Lin and Benson 2000; Sridharan and Prakash 2000). Results of these studies generally have shown that an increase in cation valence and/or electrolyte concentration (inorganic chemical solutions) or a decrease in dielectric constant (aqueous solutions of organic compounds or non-aqueous phase liquids) causes the $LL$ to decrease and the hydraulic conductivity to increase with greater effects occurring for soils containing higher activity clays such as bentonite. For example, Petrov and Rowe (1997) show that the $LL$ of a bentonite from a GCL decreased from 530% to 96% as the sodium chloride (NaCl) concentration of the testing solution increased from 0 (i.e., water) to 2.0 M, and the hydraulic conductivity of the GCL increased from $10^{-9}$ cm/s to $10^{-6}$ cm/s for the same increase in NaCl concentration.

Several studies have shown that the swell index of bentonite is directly correlated with the hydraulic conductivity of bentonite-based GCLs (Didier and Comeaga 1997; Ruhl and Daniel 1997; Lin and Benson 2000; Shackelford et al. 2000; Egloffstein 2001; Jo et
For example, the results of swell index tests on sodium bentonite from a GCL reported by Shackelford et al. (2000) and Jo et al. (2001) show that swell index of the bentonite is sensitive to the cation valence and/or electrolyte concentration in a manner that is consistent with changes in the thickness of the adsorbed layer of cations. The hydraulic conductivity of the GCL also increased when permeated with stronger electrolyte solutions (i.e., higher cation valence and/or electrolyte concentration). That is, a decrease in swell index corresponded with an increase in hydraulic conductivity, with greater decreases in swell index correlated with greater increases in hydraulic conductivity.

2.8 FLY ASH- STABILISED EXPANSIVE CLAY LINERS

Lakshmikantha and Sivapullaiah (2006) assessed the locally available materials such as kaolinitic red earth, illite and fly ash as liners for waste containment facilities. On addition of 20% bentonite to selected liner material, they found that hydraulic conductivity and adsorption capacity of the amended mixture improved. Shafique et al. (2010) investigated the long-term performance of fly ash stabilised two fine-grained soil sub bases. A low plasticity clay and a high plastic clay were stabilised with varying Class C fly ash content and statically compacted at optimum moisture content and maximum dry density and ten sets replicates were prepared and cured for 7 days. It was subjected to plasticity index tests, unconfined compression, 12 wet–dry cycles and 12 freeze–thaw cycles in a laboratory controlled environment to simulate the weathering action. They found that the effect of wet–dry cycles on stabilized soils was essentially insignificant; however, the fly ash stabilized soils lost up to 40% of the strength due to freeze–thaw cycles. They also concluded that the swell potential of stabilized expansive soils also increased due to freeze–thaw cycles.

Yang and Barbour (1992) described the change in hydraulic conductivity of a highly plastic natural clay during exposure to a concentrated sodium chloride (NaCl) solution. Hydraulic conductivity tests were carried out before and after the samples were exposed to the NaCl solutions. Scanning electron microscope photography was used to compare the soil structures before and after brine permeation. The test results showed that the alteration of hydraulic conductivity is strongly related to the initial soil structure and the
level of confining stress. They also observed that the increase in hydraulic conductivity that occurred during brine permeation could be prevented by increasing the level of confining stress.

Cey et al (2001) experimented the osmotic behaviour and hydraulic conductivity for undisturbed Cretaceous clay samples from southern Saskatchewan. Constant-head hydraulic conductivity ($k_h$) tests and osmotic flow tests was conducted over a range of pore-fluid concentrations of 0.054–1.12 equiv./L. The hydraulic conductivity of the clay increased by a factor of two as the pore-fluid concentration increased from 0.070 to 0.56 equiv./L whereas both osmotic compressibility and osmotic efficiency decreased with increasing pore-fluid concentration.

Ridley et al. (1984) found that the engineering properties of compacted fine-grained soils changed with time when exposed to a 30% NaCl brine environment. They found that the hydraulic conductivity of the brine was found to be greater than that of water in soils where the dominant clay mineral was montmorillonite, whereas a soil rich in illite and kaolinite was virtually insensitive to variations in solution composition.

This thesis is a work on new clay liner material in the form of fly ash-stabilised expansive clay. Expansive clays or montmorillonite clays are fat clays with a low hydraulic conductivity ($k$). The particle size of the montmorillonite clays is very low rendering them nearly impermeable and highly plastic (Chen, 1988). Recent research by Phanikumar and Sharma (2004) showed that, when expansive clays are stabilised with fly ash (an industrial hazardous waste), the hydraulic conductivity of the blends further reduces. The higher the density of the clay-fly ash blends, the lower would be the hydraulic conductivity (Phanikumar and Sharma, 2004). It was also found that free swell index ($FSI$), swell potential and swelling pressure of the clay-fly ash blends also decreased when fly ash content in the blends increased. This thesis presents experimental data on fly ash-stabilised expansive clay blends. Laboratory experimental studies were conducted on expansive clay-fly ash blends, which would be suggested as a new clay liner material. Important index properties such as liquid limit ($LL$), and free swell index ($FSI$) of the clay-fly ash blends were determined. Further, engineering properties such as % heave and hydraulic conductivity of the blends were also determined. Correlations between hydraulic conductivity and heave on the one hand and index properties on the
other were studied. Leachate characteristics of fly ash-stabilised expansive clay liners were also studied. The following chapters discuss in detail the experimental investigations and the test results.